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Estimation of the Dihedral Angle Between Metal Nanoparticles During Their Coalescence

A.Yu. Kolosov, D.N. Sokolov, N.Yu. Sdobnyakov*, P.V. Komarov, S.S. Bogdanov, A.A. Bogatov, V.S. Myasnichenko

Tver State University, 35, Sadovyi Per., 170002 Tver, Russia

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The process of coalescence of various metal nanoparticles has been studied by the Monte Carlo method. The interaction of nanoparticles is described by a multiparticle Gupta type potential. An algorithm of recognizing and estimating a dihedral angle at the neck is developed. The dihedral angle between metal nanoparticles during their sintering is estimated.

Keywords: Nanoparticles of gold, silver, and copper; Coalescence; Neck, dihedral angle; Monte Carlo method; Gupta potential.

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1. INTRODUCTION

The properties of nanostructured materials are determined predominantly by the specific features of interatomic interaction in their surface layers and the quantum confinement effects. Nanosized structures are of considerable interest in both fundamental and applied science. The interest in this field of science, which is among the most extensively developing fields, is related to both the fundamental physical issues and phenomena and the prospects of creating new quantum devices and systems with broad possibilities for nanoelectronics, metrology, and measurement techniques. The synthesis of nanoparticles and nanostructures, as well as experimental research in this field, is usually difficult and expensive. Theoretical approaches to the investigation of nanosystems are yet not sufficiently elaborated. This circumstance makes the development of analytical and numerical methods for predicting the properties of nanoparticles and nanomaterials as well as for monitoring processes in these systems an especially topical task.

Nanoclusters in a condensed state possess physical characteristics different from those of the corresponding macroscopic crystals. In addition, nanoclusters exhibit new optical and magnetic properties dependent not only on their size, but also on the mode of organization or self-organization. In this context, there appear tasks related to reduction in sizes of systems and control over their structures. In particular, a decrease in dimensions of elements for microelectronics leads to problems related to the creation of nanocontacts and nanowires [1, 2], which must possess both high structural stability and sufficient electric conductivity so as to meet requirements of the new stage of technology development. Creation of new magnetic memory devices, nanodiodes, nanowires, etc. poses the problem of controlled synthesis and organization of nanoclusters. In this respect, the ability of predicting and controlling the size and structure of nanoparticles becomes very important, since the arrangement of atoms is a key factor that determined the properties of these particles and influences the strength and elasticity of related nanostructures. Coalescence is among the processes that can be used for controlling the structure and dimensions of particles.

There are three mechanisms involved in the process of nanoparticle formation in an inert gas medium: coagulation, coalescence, and aggregation on a small cluster-nucleus. The knowledge of a dominating mechanism and peculiarities of each one under given external conditions provides a basis that allows us to control the structure and size of particles.

According to Arcidiacono et al. [3], the coalescence of two nanoparticles can be characterized by the two main stages:

(i) The first stage is very fast and involves the formation of a neck region between particles and its growth by the exponential law:

$$\left(\frac{x}{r_p}\right)^n = \frac{Bt}{r_p^m}, \tag{1}$$

where r_p is the initial particle radius, x is the neck radius, t is the time, B is the temperature-dependent constant coefficient, and n, m are power exponents. This process depends neither on the radii of particles nor on the initial temperature. The first stage duration amounts up to 0.3 ns.

(ii) The second stage involves disappearance of the neck with the formation of a coalesced particle.

In order to explain the process of neck formation and growth during coalescence, Asoro et al. [4] suggested that the neck growth at early stage proceeds due to decreasing chemical potential at the point of contact between particles.

By measuring a dihedral angle at the neck, it is possible to calculate the driving force of coalescence and define the onset of particle growth via coalescence. In the equilibrium state, the dihedral angle can be expressed as follows

$$\gamma_{gb} = 2\gamma_s \cos(\psi/2), \tag{2}$$

where γ_{gb} is the energy of the grain boundary and γ_s is the surface energy.

In the case under consideration, the neck growth proceeds as long as $\psi < \psi_{eq}$, while the growth by grain boundary motion proceeds until the dihedral angle will reach its equilibrium value that is attained at the final stage of coalescence (Fig. 1).

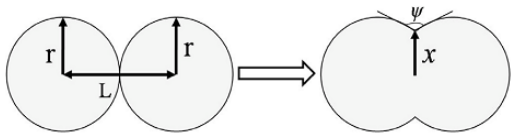

Fig. 1 – Scheme of the coalescence of two spherical particles: r is the particle radius; L is the distance between centers of particles; x is the neck radius; ψ is the dihedral angle

2. METHOD OF INVESTIGATION

The present study was aimed at modeling the coalescence of two spherical particles of various metals and determining the dihedral angle during their sintering. For this purpose, we have developed a special algorithm of recognizing a dihedral angle at the neck and estimating its value. This algorithm is briefly as follows:

1. The system is centered so that one particle would occur in the negative part, and the other in the positive part of axis X;

2. Plane $z = 0$ is considered, and all atoms occurring in its certain vicinity are recognized and projected onto this plane;

3. Highest atoms in the left and right cluster are determined, and only atoms occurring within the interval of axis X between these highest atoms are considered;

4. Attempt at recognizing the dihedral angle is made by selecting pairs of atoms in each cluster and drawing lines via them, so that all atoms would be beneath these lines. Then, the angle between lines passing over the left and right clusters is calculated. To eliminate ambiguity, the angles obtained for various pairs of lines are averaged.

5. Clusters are rotated about axis X by certain angle φ_x, steps **1-4** are repeated, and statistics for final estimation of the dihedral angle is thus accumulated.

In the present work, the process of coalescence (including the parameters of growing neck region) of nanoclusters having various sizes was studied for nanoparticles of gold, silver, and copper by Monte Carlo method with the interatomic interaction described by a multiparticle Gupta potential [5]. The evolution of nanoparticles with varying temperature and diameter was numerically simulated using a computational scheme developed previously [6, 7] based on the Metropolis algorithm [8].

3. ANALYSIS OF RESULTS

The numerical simulations of coalescence were performed for three systems of nanoparticles: $Au_{381} - Au_{381}$, $Cu_{381} - Cu_{381}$, and $Au_{381} - Ag_{381}$. The dihedral angles were determined at temperatures close to the melting points, which were set to be 894 K for distances within 0.0-0.3 nm and 1026 K for distances within 0.6-0.9 nm. This difference is related to the fact that the coalescence at greater distances takes place at higher temperatures because only nanoparticles whose spacing does not exceed the saturation radius of a metallic potential (< 6 Å) can fall into the contact zone. The dihedral radius was analyzed using the algorithm described above and the accumulated statistics was averaged for each system.

Fig. 2 shows an example of the construction and analysis of the dihedral angle between nanoparticles in the $Cu_{381} - Cu_{381}$ system at a temperature of 894 K.

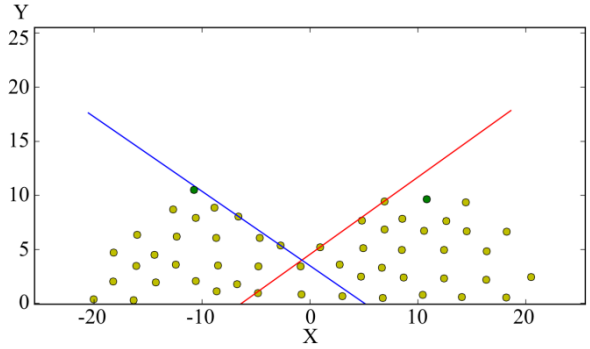

Fig. 2 – Analysis of the dihedral angle between Cu_{381} nanoparticles at a temperature of 894 K (dihedral angle, $\psi = 109.9°$; initial distance between nanoparticles, 0.0 nm)

In all the three cases studied, the process of neck formation proceeded in a similar manner despite the difference of metals in these systems. The average square deviation of the dihedral angle in all systems amounted to $\sigma = \pm 12°$. An increase in the initial spacing of nanoparticles led to growth in the dihedral size and in the relative size of the neck region. Tables 1-3 present the parameters of all systems of two nanoparticles during coalescence. An analysis of these data shows that increase in the relative size of the neck is accompanied by decreasing ratio of the grain boundary

Table 1 – Calculated values of the relative size of the neck and dihedral angle at the neck for the $Cu_{381} - Cu_{381}$ system in the vicinity of the melting temperature

Parameter	$d = 0.0$ nm	$d = 0.3$ nm	$d = 0.6$ nm	$d = 0.9$ nm
x/r	0.52	0.54	0.43	0.67
ψ, °	113	115	117	135
γ_{gb}/γ_s	1.1	1.07	1.05	0.77

Table 2 – Calculated values of the relative size of the neck and dihedral angle at the neck for the $Au_{381} - Au_{381}$ system in the vicinity of the melting temperature

Parameter	$d = 0.0$ nm	$d = 0.3$ nm	$d = 0.6$ nm	$d = 0.9$ nm
x/r	0.6	0.61	0.64	0.68
ψ, °	118	120	142	144
γ_{gb}/γ_s	1.03	0.99	0.65	0.62

Table 3 – Calculated values of the relative size of the neck and dihedral angle at the neck for the $Au_{381}-Au_{381}$ system in the vicinity of the melting temperature

Parameter	$d=0.0$ nm	$d=0.3$ nm	$d=0.6$ nm	$d=0.9$ nm
x/r	0.55	0.56	0.61	0.64
$\psi,^\circ$	113	114	117	122
γ_{gb}/γ_s	1.1	1.08	1.05	0.97

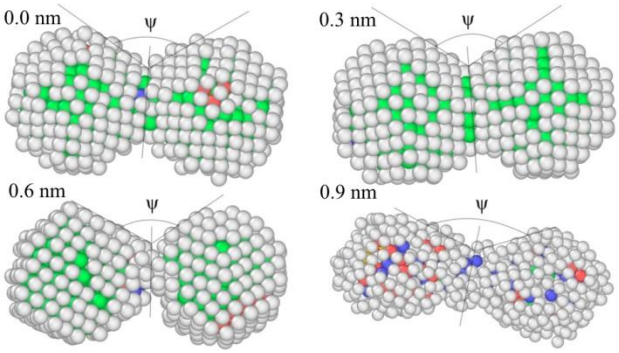

Fig. 3 – Instantaneous configurations of the $Cu_{381}-Cu_{381}$ system for various initial distances between nanoparticles, with indicated results of structure analysis. Green, blue, and red atoms correspond to fcc, bcc, and hcp lattices, respectively

energy to surface energy. Fig. 3 shows instantaneous configurations of the $Cu_{381}-Cu_{381}$ system for various initial distances between nanoparticles, with indicated dihedral angles.

In all the three systems studied, nanoparticles had the crystalline lattice orientation (001). However, it should be noted that variations in the lattice orientation play significant role in the process of neck formation. однако. In the sphere-sphere system with (101) lattice orientation, the melting temperature of the system decreases on the average by 30 K, but the system energy upon coalescence increases. In this case, the neck is formed slower and at higher temperatures, with decreasing contact area and dihedral angle (see Fig. 4).

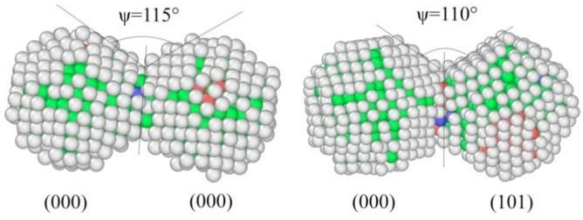

Fig. 4 – Comparison of dihedral angles in the $Cu_{381}-Cu_{381}$ system for different lattice orientations in one of the nanoparticles. Initial distance between nanoparticles,0.3 nm. Green, blue, and red atoms correspond to fcc, bcc, and hcp lattices, respectively

For some other systems, in particular, those with lattice orientations (001), (101) and (011) in one particle, the energy decreases at distances where the coalescence proceeds prior to melting. This is due to the appearance of surface defects and the resulting fracture of the crystalline lattice. The process is usually accompanied by the rotation of either one particle or the whole system. In these cases, the neck is formed faster, with significant increase in the area of contact and dihedral angle between nanoparticles. Fig. 5 shows an example of this behavior for the $Cu_{627}-Cu_{627}$ system. Here, the lattice orientation does not influence the fact that the ratio of the grain boundary energy to the surface energy decreases with increasing relative size of the neck.

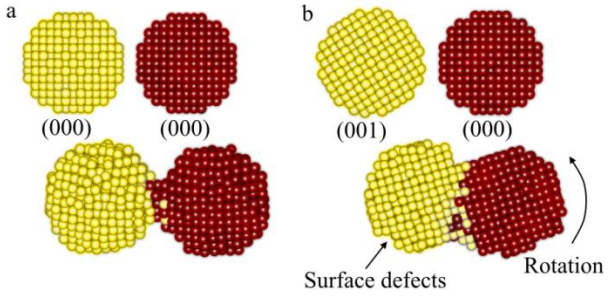

Fig. 5 – Instantaneous configurations of the $Cu_{627}-Cu_{627}$ system during coalescence at temperatures (a) 293 K and (b) 909 K. Initial distance between nanoparticles, 0.3 nm

4. CONCLUSION

Analysis of the obtained results showed that the orientation of crystalline lattices and the initial distance between nanoparticles influence the subsequent coalescence process and the strength of a neck formed in the system, which is an important factor for nanocontacts. Geometric parameters of the neck (dihedral angle, effective length) depend on the distance between nanoparticles in the initial configuration and on the orientation of crystalline lattices. In addition, these factors also influence the temperature at which the neck is formed and the temperature at which complete sintering of nanoparticles takes place.

In the framework of this research, we have created and described an algorithm for estimation of the dihedral angle and used this algorithm to calculate the relative neck size and dihedral angles for systems of spherical gold, silver, and copper nanoparticles. It is established that an increase in the relative neck size is accompanied by decrease in the ratio of the grain boundary energy to the surface energy and that this dependence is not significantly influenced by orientation of the crystalline lattices of nanoparticles.

It should be noted that the rate of the coalescence process depends on the interfacial tension and the corresponding dimensional effects [9]. In the framework of our approach described previously [10, 11], it was shown that the presence of interfaces is additional factor favoring the stability of such nanosystems.

In a similar example [12], dominating mechanisms of sintering have been investigated using molecular

dynamics simulations based on the embedded-atom method for copper nanoparticles. One of the main results in [12] is that the particle rotation during sintering is mainly induced by grain boundary torque with grain boundary diffusion and rarely by dislocation. This coincides with the result obtained in our simulations by Monte-Carlo method. The problem of description of the shape of a neck formed in the coalescence process has been discussed in our work [13] and in a later work [14]. The models used in [13, 14] provide, in our opinion, a rather simple analytical description of coalescence between nanoparticles, which is independent of their constituent elements or crystal orientations. Thus, the proposed methodology of recognizing and estimating a dihedral angle at the neck, together with results presented in [13, 14], allow us to more accurately describe the dynamics of changes in shape of the neck during coalescence.

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REFERENCES

1. A.L. Klavsyuk, S.V. Kolesnikov, E.M. Smelova, A.M. Saletsky, *Phys. Sol. State* **53**, 2356 (2011).
2. A.L. Klavsyuk, S.V. Kolesnikov, E.M. Smelova, A.M. Saletsky, *J. Exp. Theor. Phys. Let.* **91**, 158 (2010).
3. N.R. Arcidiacono, S. Bieri, D. Poulikakos, C.P. Grigoropoulos, *Int. J. Multiph. Flow* **30**, 979 (2004).
4. M.A. Asoro, D. Kovar, Y. Shao-Horn, L.F. Allard, P.J. Ferreira, *Nanotechnology* **21**, 025701 (2010).
5. R.P. Gupta, *Phys. Rev. B* **23**, 6265 (1981).
6. A.Yu. Kolosov, N.Yu. Sdobnyakov, V.S. Myasnichenko, D.N. Sokolov, *J. Surf. Invest.: X-ray, Synchrotron Neutron Tech.* **10**, 1292 (2016).
7. A.Yu. Kolosov, N.Yu. Sdobnyakov, P.V. Komarov, N.V. Novozhilov, A.N. Bazulev, D.N. Sokolov, *Phys. Chem. Asp. Res. Clust., Nanostr. and Nanomat.: Interuniv. Coll. Sci. Papers* **5**, 134 (2013).
8. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.N. Teller, E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
9. A.N. Bazulev, V.M. Samsonov, N.Yu. Sdobnyakov, *Russ. J. Phys. Chem. A.* **76**, 1872 (2002).
10. V.M. Samsonov, N.Yu. Sdobnyakov, *Centr. Eur. J. Phys.* **1**, 344 (2003).
11. V.M. Samsonov, N.Yu. Sdobnyakov, A.N. Bazulev, *Surf. Sci.* **532-535**, 526 (2003).
12. Y. Seong, Y. Kim, R. German, S. Kim, S.-G. Kim, S.J. Kim, H.J. Kim, S.J. Park, *Comp. Mat. Sci.* **123**, 164 (2016).
13. N.Yu. Sdobnyakov, D.N. Sokolov, E.M. Kozlova, T.M. Neverova, A.Yu. Kolosov, *Herald of Tver St. Univer. Series: App. Math.* **1**, 5 (2014).
14. P. Grammatikopoulos, E. Toulkeridou, K. Nordlund, M. Sowwan, *Model. Simul. Mat. Sci. Engin.* **23**, 015008 (2015).